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## 5.—CHEMICAL INVESTIGATION OF THE EXTRACTIVES OF TWO WESTERN AUSTRALIAN WOODS.

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## (1) THE OLEO-RESIN OF MYOPORUM SERRATUM.

Myoporum serratum (N.O. Myoporineae) is a species found growing on the Eastern Goldfields, where it is commonly known as "Dogwood." The tree attains a height of 20 feet and a d'ameter of 6 to 8 inches, and is said to be available in considerable quantities. The wood, even when green, burns with a bright flame, giving off a dense black smoke and characteristic odour. This and the rather pleasant sweetish aromatic odour of the wood indicate the presence of a considerable amount of oil. In 1930 a section of a log was forwarded to the Government Chemical Laboratory by the Conservator of Forests (Mr. S. L. Kessell) with a view to determining if it carried any essential oil or other extractive matter which might have some economic value.

The log consisted of 2½in. to 3in. of heartwood, which was brown in colour, surrounded by about 1¾in. of yellowish white sapwood. The heartwood possessed the strongest perfume. After de-barking the log was reduced to sawdust, which had a distinctly oily feel. On continuous extraction the comminuted wood yielded:—

to petroleum ether (B.P. 40-50°) ... ... 3.4% to acetone ... ... ... ... ... 12.0%

In both cases the extract was a semi-fluid, sticky, red oil.

Steam distillation of about 1 kilogram of wood yielded 0.65% of a brown, sticky, resinous material.

Petroleum ether being the best solvent for the oils (acetone extracting much other extractive matter including resins) a considerable quantity of the comminuted wood (900 grms.) was exhausted by the former solvent, yielding 28.1 grams of a viscous dark red oil. This and the steam distillate were examined with the following results:—

| were examined with             |         |     | Petroleum ether extract.                                | Steam distillate.                           |
|--------------------------------|---------|-----|---|---|
| Odour                          | •••     | ••• | Rather sickly aromate casionally a faint of sandalwood. | tic odour, with oc-<br>odour reminiscent of |
| Refractive index $n_D^{20}$    |         |     | 1.5439  | 1.5165                                      |
| Solubility in 90 per cent. a   | lcohol  |     | Sol. in 2 vols.   | Sol. in 1 vol.                              |
| Saponification number          |         |     | 27  | 194   |
| Acid value                     |         |     | 4   | 59  |
| Ester value                    |         |     | 23  | 135   |
| Saponification value of the ac | etvlate |     | 144   |   |
| Unsaponifiable matter          | •••     | ••• | 81.4 per cent.  | 42·1 per cent.                              |

A small quantity of phenolic or acidic constituents (6.2%), as determined by extraction of an ethereal solution with 10% caustic soda solution, was found in the petroleum ether extract.

Distillation: The petroleum ether extract on distillation under reduced pressure (30 m.m.) yielded over 50% of a pale yellow oil, B.P. 200-220°C., which on exposure to air changed in colour to a bright green. This possessed the characterisic odour of the wood and its extract. Its reactions indicated it to be an unsaturated hydroxyl compound probably of an alcoholic nature. The residue after distillation was a hard, dark red resin.

Summary: The wood of *Myoperum serratum* was found to contain 3.4 per cent. of an oil or oleo-resin extractable by petroleum ether. Steam distillation yielded 0.65 per cent. of oleo-resin, and acetone extracted 12.0 per cent., which included a considerable quantity of resin.

The oleo-resin consists of a high boiling point oil together with a hard, brittle, dark red resin. The odoriferous principle of the wood appears to reside in the fraction boiling at 200°-220°C. (30 m.m.) and may be a terpene or sesquiterpene alcohol.

The oil or oleo resin may have some value as a fixative in perfumery, but at present no other economic use for it can be suggested.

## (2) THE OIL AND COLOURING MATTER OF THE STEM OF ACACIA ACUMINATA.

Acacia acuminata is a tree attaining a height of 30 to 40 feet, but usually under 20 feet. It is indigenous to Western Australia, where it is widely distributed, especially in the drier areas east of the Darling Ranges. It is plentiful in parts of the wheat belt, where the durability of the wood and its resistance to the attacks of white ants have resulted in its extensive use for fencing posts. The timber is one of the hardest, heaviest and most ornamental of Australian woods.

The common name, "raspberry jam" or "jam" is derived from the odour of the wood, which is similar to that of *Rubus indaeus*, the common raspberry. The odorous principle persists for years in specimens of the wood, but is most evident in the freshly cut timber. The presence of essential oil in the wood is indicated by the phenomenon of "sweating" or exudation of oil which has been observed to take place, especially from the heartwood.

This investigation was commenced with the object of gaining some information on the essential oil and the nature of the odorous constituent of the wood. No published record appears of any work having been done on this subject. The Forests Products Laboratory in Perth some years ago commenced an investigation. Steam distillation was tried with, it is understood, not very satisfactory results, but the work was not proceeded with.

The results of the present investigations were disappointing in regard to yield, the lowness of which, with the facilities at present available, made the separation and isolation of the constituents of the oil impossible. It was felt, however, that the results, which give indications of the nature of the oil and the colouring matter of the wood, should be published, and that later, if the means and time become available, further detailed examination might be undertaken. The work was carried out on portion of a log kindly supplied by the Conservator of Forests (Mr. S. L. Kessell).

Microscopic examination of the wood of A. acuminata shows the heart-wood to be plentifully scattered with pores. These are vessels or tracheae that have become closed and are in most cases filled with a dark red deposit which appears to be of an oleo-resinous nature. This also appears throughout the parenchymatous tissue.

Extraction of oil: The log consisted of about 5in. of heartwood which was brown in colour, surrounded by about 1in. of yellowish sapwood and 3sin. of bark. It was de-barked and reduced to shreds in a pulveriser. Extraction with light petroleum ether (B.P. 30°-50°C.) was carried out at room temperature by percolation, this being considered less likely to decompose the constituents of the oil. The extract was evaporated at a temperature not exceeding 60deg. C., the last remains of the solvent being removed under reduced pressure. The odorous principles did not appear to be volatile with the solvent at the temperatures employed.

Properties of the extract: Petroleum ether extracted 0.34% of a sticky, bright red (carrotty) paste, having a typical sweetish woody odour with a secondary odour of raspberries. The latter was fugitive, and was more noticeable from traces of the extract than the more concentrated form. The extract burned with a bright smoky flame, giving off a resinous odour. It was

A portion of the disintegrated wood which had been kept in the laboratory for eight or nine months yielded practically no coloured extract to petroleum ether, but considerable reddish brown colour to acetone and to alcohol, indicating that the carotene had become changed. This was not surprising in view of the instability of carotene and the avidity with which it absorbs oxygen.

It is interesting to note that Schmid & Pietsch (Chem. Abs. 1931.25. 4276) found the yellow alcohol soluble colouring matter of the "common acacia" wood to be a flavone.

The fact that carotene is closely related chemically to ionone, the chief odorous constituent of several essential oils, may possibly have some bearing on the chemical nature of the essential oil of A. acuminata.

I wish to thank the Government Mineralogist and Analyst (Dr. E. S. Simpson) for permission to publish the results of this work.

soluble in sulphuric ether, benzene, chloroform, and acetone, giving a deep orange-yellow solution. It possessed the following characteristics:—Refractive index  $n_{\rm D}^{50}$  1.515; saponification number nil, slightly soluble in 90% alcohol.

Reactions of the extract: The material, of which only a few grams were available, reacted strongly with bromine and iodine, indicating the presence of unsaturated compounds. A characteristic and beautiful colour reaction was obtained when one or two drops of concentrated sulphuric acid were allowed to flow into the solution of a small quantity in acetic anhydride. The solution turned emerald green, rapidly changing to deep blue. A similar reaction is given by the sesquiterpene cadinene in chloroform solution, the blue changing to red on heating, however, which is not so with the material under question. The extract dissolved in concentrated sulphuric acid with a blue colour. Its solution in chloroform gave a blue colouration with antimony trichloride and with zinc chloride. The solution in absolute alcohol deposited on standing a small amount of what appeared to be a stearoptene or paraffin.

Nature of the oil: The reactions and properties of the extracted oil indicate that the principal constituents are of a terpene or sesquiterpene nature with probably a stearoptene present. The odorous principle, as is to be expected, has no chemical relation to that of the raspberry, which is chiefly composed of esters. The odorous constituents of the wood of A. acuminata are unchanged by extraction and persist in the unsaponifiable portion.

The resin: The acetone extract from the wood was found to be hard, brittle, dark red resin, soluble in alcohol, and having a saponification number of 255.

The presence of Carotene: The solution yielded by the wood to petroleum ether and other organic solvents had a bright orange-yellow colour. The concentrated extract possessed strong tinctorial power, and stained objects a bright yellow. The colouring matter, however, was not soluble in water or in aqueous solutions of acids or alkalis. Prolonged boiling with 6% hydrochloric acid solution yielded no hydrolysis products giving coloured solutions with acids or alkalis. It did not, therefore, belong to either the anthocyanin or anthoxanthin group of plant pigments, but appeared to be a carotinoid or lipochrome. Further examination showed the colouring matter to resemble carotene in the following respects:—solubilities, non-extractability with 80% alcohol from petroleum ether solutions, and rapid fading of solutions in bright sunlight. The visual absorption spectrum showed bands in the region of the two bands in the blue violet end of the spectrum given by carotene. Carotene and vitamin A, its derivative, both give the blue colour in chloroform solution with antimony trichloride and zinc chloride mentioned above, a reaction which is considered specific for them.

On standing, the pasty petroleum ether extract of the wood deposited numerous tiny tabular pleochroic crystals. These showed considerable resemblance to the intracellular specks of carotene seen in the root of the carrot and to carotene extracted therefrom. There is little doubt that a considerable portion of the colouring matter in the stem of A. acuminata consists of the pigment carotene. It appears to be dissolved in the oil held in the pores, and no microscopic crystals have been noted in the wood.